

Saturated Zone Denitrification: Potential for Natural Attenuation of Nitrate Contamination in Shallow Groundwater Under Dairy Operations

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We present results from field studies at two central California dairies that demonstrate the prevalence of saturated-zone denitrification in shallow groundwater with $^3\text{H}/^3\text{He}$ apparent ages of <35 years. Concentrated animal feeding operations are suspected to be major contributors of nitrate to groundwater, but saturated zone denitrification could mitigate their impact to groundwater quality. Denitrification is identified and quantified using N and O stable isotope compositions of nitrate coupled with measurements of excess N_2 and residual NO_3^- concentrations. Nitrate in dairy groundwater from this study has $\delta^{15}\text{N}$ values (4.3–61‰), and $\delta^{18}\text{O}$ values (–4.5–24.5‰) that plot with $\delta^{18}\text{O}/\delta^{15}\text{N}$ slopes of 0.47–0.66, consistent with denitrification. Noble gas mass spectrometry is used to quantify recharge temperature and excess air content. Dissolved N_2 is found at concentrations well above those expected for equilibrium with air or incorporation of excess air, consistent with reduction of nitrate to N_2 . Fractionation factors for nitrogen and oxygen isotopes in nitrate appear to be highly variable at a dairy site where denitrification is found in a laterally extensive anoxic zone 5 m below the water table, and at a second dairy site where denitrification occurs near the water table and is strongly influenced by localized lagoon seepage.

Introduction

High concentrations of nitrate, a cause of methemoglobinemia in infants (1), are a national problem in the United States (2), and nearly 10% of public drinking water wells in the state of California are polluted with nitrate at concentrations above the maximum contaminant level (MCL) for drinking water set by the U.S. Environmental Protection Agency (3). The federal MCL is 10 mg/L as N, equivalent to the California EPA limit of 45 mg/L as NO_3^- (all nitrate concentrations are hereafter given as NO_3^-). In the agricultural areas of California's Central Valley, it is not uncommon

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to have nearly half the active drinking water wells produce groundwater with nitrate concentrations in the range considered to indicate anthropogenic impact (>13–18 mg/L) (2, 4). The major sources of this nitrate are septic discharge, fertilization using natural (e.g., manure) or synthetic nitrogen sources, and concentrated animal feeding operations. Dairies are the largest concentrated animal operations in California, with a total herd size of 1.7 million milking cows (5).

Denitrification is the microbially mediated reduction of nitrate to gaseous N_2 , and can occur in both unsaturated soils and below the water table where the presence of NO_3^- , denitrifying bacteria, low O_2 concentrations, and electron donor availability exist. In the unsaturated zone, denitrification is recognized as an important process in manure and fertilizer management (6). Although a number of field studies have shown the impact of denitrification in the saturated zone (e.g., 7, 8–11), prior to this study it was not known whether saturated zone denitrification could mitigate the impact of nitrate loading at dairy operations. The combined use of tracers of denitrification and groundwater dating allows us to distinguish between nitrate dilution and denitrification, and to detect the presence of pre-modern water at two dairy operations in the Central Valley of California, referred to here as the Kings County Dairy (KCD) and the Merced County Dairy (MCD; Figure 1). Detailed descriptions of the hydrogeologic settings and dairy operations at each site are included as Supporting Information.

Materials and Methods

Concentrations and Nitrate Isotopic Compositions. Samples for nitrate N and O isotopic compositions were filtered in the field to 0.45 μm and stored cold and dark until analysis. Anion and cation concentrations were determined by ion chromatography using a Dionex DX-600. Field measurements of dissolved oxygen and oxidation reduction potential (using Ag/AgCl with 3.33 mol/L KCl as the reference electrode) were carried out using a Horiba U-22 water quality analyzer. The nitrogen and oxygen isotopic compositions ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) of nitrate in 23 groundwater samples from KCD and MCD were measured at Lawrence Berkeley National Laboratory's Center for Isotope Geochemistry using a version of the denitrifying bacteria procedure (12) as described in Singleton et al. (13). In addition, the nitrate from 17 samples was extracted by ion exchange procedure of (14) and analyzed for $\delta^{15}\text{N}$ at the University of Waterloo. Analytical uncertainty (1σ) is 0.3‰ for $\delta^{15}\text{N}$ of nitrate and 0.5‰ for $\delta^{18}\text{O}$ of nitrate. Isotopic compositions of oxygen in water were determined on a VG Prism isotope ratio mass spectrometer at Lawrence Livermore National Laboratory (LLNL) using the CO_2 equilibration method (15), and have an analytical uncertainty of 0.1‰.

Membrane Inlet Mass Spectrometry. Previous studies have used gas chromatography and/or mass spectrometry to measure dissolved N_2 gas in groundwater samples (16–19). Dissolved concentrations of N_2 and Ar for this study were analyzed by membrane inlet mass spectrometry (MIMS), which allows for precise and fast determination of dissolved gas concentrations in water samples without a separate extraction step, as described in Kana et al. (20, 21). The gas abundances are calibrated using water equilibrated with air under known conditions of temperature, altitude, and humidity (typically 18 °C, 183 m, and 100% relative humidity). A small isobaric interference from CO_2 at mass 28 (N_2) is corrected based on calibration with CO_2 -rich waters with known dissolved N_2 , but is negligible for most samples. Samples are collected for MIMS analysis in 40 mL amber

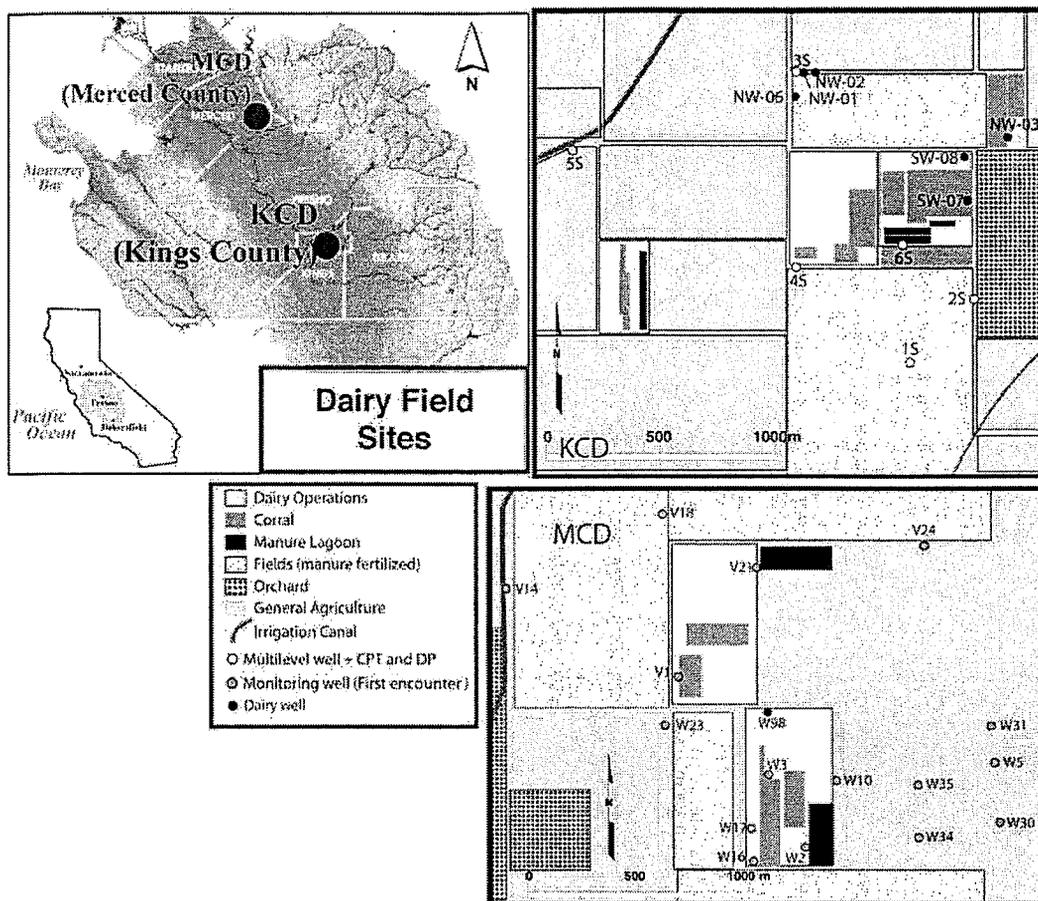


FIGURE 1. Location of dairy study sites, and generalized maps of each dairy showing sample locations relative to lagoons and dairy operations.

glass VOA vials with no headspace that are kept cold during transport, and then analyzed within 24 h.

Noble Gases and $^3\text{H}/^3\text{He}$ Dating. Dissolved noble gas samples are collected in copper tubes, which are filled without bubbles and sealed with a cold weld in the field. Dissolved noble gas concentrations were measured at LLNL after gas extraction on a vacuum manifold and cryogenic separation of the noble gases. Concentrations of He, Ne, Ar, and Xe were measured on a quadrupole mass spectrometer. The ratio of ^3He to ^4He was measured on a VG5400 mass spectrometer. Calculations of excess air and recharge temperature from Ne and Xe measurements are described in detail in Ekwurzel (22), using an approach similar to that of Aeschbach-Hertig et al. (23).

Tritium samples were collected in 1 L glass bottles. Tritium was determined by measuring ^3He accumulation after vacuum degassing each sample and allowing 3–4 weeks accumulation time. After correcting for sources of ^3He not related to ^3H decay (24, 25), the measurement of both tritium and its daughter product ^3He allows calculation of the initial tritium present at the time of recharge, and apparent ages can be determined from the following relationship based on the production of tritogenic helium ($^3\text{He}_{\text{trit}}$):

$$\text{Groundwater Apparent Age (years)} = -17.8 \times \ln(1 + ^3\text{He}_{\text{trit}}/^3\text{H})$$

Groundwater age dating has been applied in several studies of basin-wide flow and transport (25–27). The reported groundwater age is the mean age of the mixed

sample, and furthermore, is only the age of the portion of the water that contains measurable tritium. Average analytical error for the age determinations is ± 1 year, and samples with ^3H that is too low for accurate age determination (< 1 pCi/L) are reported as > 50 years. Significant loss of ^3He from groundwater is not likely in this setting given the relatively short residence times and high infiltration rates from irrigation. Apparent ages give the mean residence time of the fraction of recently recharged water in a sample, and are especially useful for comparing relative ages of water from different locations at each site. The absolute mean age of groundwater may be obscured by mixing along flow paths due to heterogeneity in the sediments (28).

Results and Discussion

Nitrate in Dairy Groundwater. Nitrate concentrations at KCD range from below detection limit (BDL, < 0.07 mg/L) to 274 mg/L. Within the upper aquifer, there is a sharp boundary between high nitrate waters near the surface and deeper, low nitrate waters. Nitrate concentrations are highest between 6 and 13 m below ground surface (BGS) at all multilevel wells (0.5 m screened intervals), with an average concentration of 98 mg/L. Groundwater below 15 m has low nitrate concentrations ranging from BDL to 2.8 mg/L, and also has low or nondetectable ammonium concentrations. The transition from high to low nitrate concentration corresponds to decreases in field-measured oxidation–reduction potential (ORP) and dissolved oxygen (DO) concentration. ORP values are generally above 0 mV and DO concentrations are > 1 mg/L in the upper 12 m of the aquifer, defining a more oxidizing zone (Figure 2). A reducing zone is indicated below

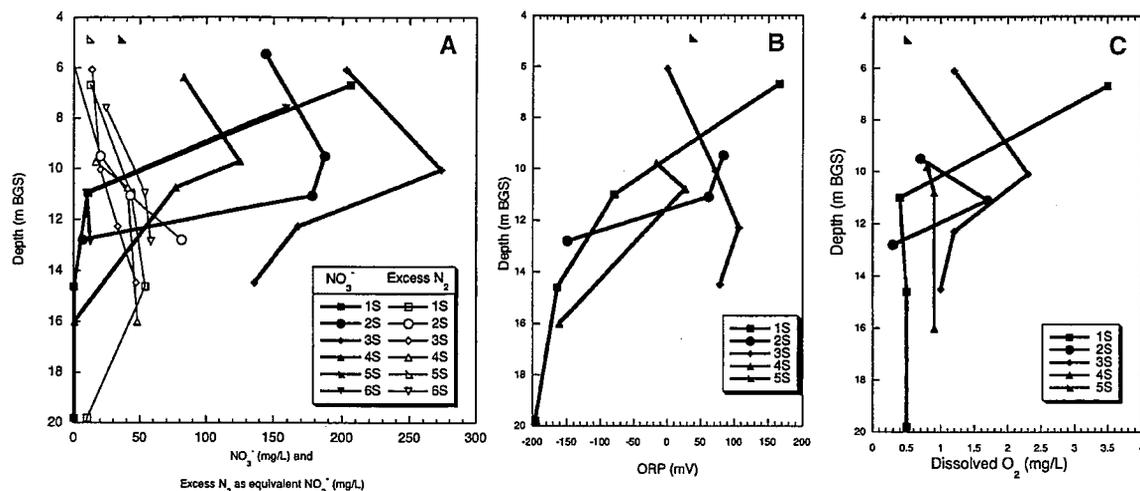


FIGURE 2. (A) Average excess N_2 and nitrate concentrations, (B) oxidation-reduction potential (ORP), and (C) dissolved oxygen in multilevel monitoring wells at the KCD site.

12 m by ORP values as low as -196 mV and DO concentrations <1.2 mg/L. Vertical head varies by less than 10 cm in the upper aquifer multilevel wells.

Nitrate concentrations at MCD monitoring wells sampled for this study range from 2 to 426 mg/L with an average of 230 mg/L. Several wells (W-02, W-16, and W-17) located next to a lagoon and corral have lower nitrate but high ammonium concentrations (Table 1 in Supporting Information). The MCD wells are all screened at the top of the unconfined aquifer except W98, a supply well that is pumped from approximately 57 m BGS. Nitrate concentrations observed for this deeper well are <1 mg/L.

Dissolved Gases. Nitrogen gas, the comparatively conservative product of denitrification, has been used as a natural tracer to detect denitrification in the subsurface (16–18). Groundwater often also contains N_2 beyond equilibrium concentrations due to incorporation of excess air from physical processes at the water table interface (23, 29, 30). In the saturated zone, total dissolved N_2 is a sum of these three sources:

$$(N_2)_{\text{dissolved}} = (N_2)_{\text{equilibrium}} + (N_2)_{\text{excess air}} + (N_2)_{\text{denitrification}}$$

By normalizing the measured dissolved concentrations as N_2/Ar ratios, the amount of excess N_2 from denitrification can be calculated as

$$(N_2)_{\text{denitrification}} = \left(\frac{N_2}{Ar} \right)_{\text{measured}} - \left(\frac{N_{2\text{equilibrium}} + N_{2\text{excess air}}}{Ar_{\text{equilibrium}} + Ar_{\text{excess air}}} \right) Ar_{\text{measured}}$$

where the N_2 and Ar terms for equilibrium are calculated from equilibrium concentrations determined by gas solubility. The N_2/Ar ratio is relatively insensitive to recharge temperature, but the incorporation of excess air must be constrained in order to determine whether denitrification has shifted the ratio to higher values (19). Calculations of excess N_2 based on the N_2/Ar ratio assume that any excess air entrapped during recharge has the ratio of N_2/Ar in the atmosphere (83.5). Any partial dissolution of air bubbles would lower the N_2/Ar ratio (30, 31), thus decreasing the apparent amount of excess N_2 .

For this study, Xe and Ne derived recharge temperature and excess air content were determined for 12 of the monitoring wells at KCD and 9 wells at MCD. For these sites, excess N_2 can be calculated directly, accounting for the contribution of excess air and recharge temperature. Site

representative mean values of recharge temperature and excess air concentration are used for samples without noble gas measurements. Mean annual air temperatures at the KCD and MCD sites are 17 and 16 °C, respectively (32), and the Xe-derived average recharge temperatures for the KCD and MCD sites are 19 and 18 °C. Recharge temperatures are most likely higher than mean annual air temperature because most recharge is from excess irrigation during the summer months. The average amount of excess air indicated by Ne concentrations is 2.2×10^{-3} cm³(STP)/g H₂O for KCD and 1.7×10^{-3} cm³(STP)/g H₂O for MCD. From these parameters, we estimate the site representative initial N_2/Ar ratios including excess air to be 41.2 for KCD and 40.6 for MCD. Measured N_2/Ar ratios greater than these values are attributed to production of N_2 by denitrification.

The excess N_2 concentration can be expressed in terms of the equivalent reduced nitrate that it represents in mg/L NO_3^- based on the stoichiometry of denitrification. Considering excess N_2 in terms of equivalent NO_3^- provides a simple test to determine whether there is a mass balance between nitrate concentrations and excess N_2 . From Figure 2, there does not appear to be a balance between nitrate concentrations and excess N_2 in KCD groundwater, since nitrate concentrations in the shallow wells are more than twice that of equivalent excess N_2 concentrations in the anoxic zone. There are multiple possible causes of the discrepancy between NO_3^- concentrations and excess N_2 concentrations including (1) the NO_3^- loading at the surface has increased over time, and denitrification is limited by slow vertical transport into the anoxic zone, (2) mixing with deeper, low initial NO_3^- waters has diluted both the NO_3^- and excess N_2 concentrations, or (3) some dissolved N_2 has been lost from the saturated zone. All three processes may play a role in N cycling at the dairies, but we can shed some light on their relative importance by considering the extent of denitrification and then constraining the time scale of denitrification as discussed in the following sections.

Isotopic Compositions of Nitrate. Large ranges in $\delta^{15}N$ and $\delta^{18}O$ values of nitrate are observed at both dairies (Figure 3). Nitrate from KCD has $\delta^{15}N$ values of 4.3–61.1‰, and $\delta^{18}O$ values of -0.7 –24.5‰. At MCD, nitrate $\delta^{15}N$ values range from 5.3 to 30.2‰, and $\delta^{18}O$ values range from -0.7 to 13.1‰. The extensive monitoring well networks at these sites increase the probability that water containing residual nitrate from denitrification can be sampled.

Nitrate $\delta^{15}N$ and $\delta^{18}O$ values at both dairies are consistent with nitrification of ammonium and mineralized organic N

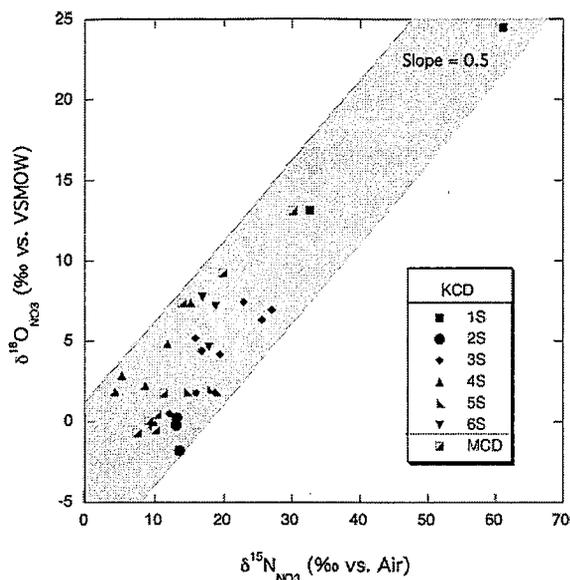


FIGURE 3. Oxygen and nitrogen isotopic composition of nitrate in dairy groundwater from multilevel monitoring wells at KCD and first encounter wells at MCD. The shaded region indicates a slope of 0.5 for a range of starting compositions. Calculated slopes for linear fits to multilevel wells at KCD and first encounter wells at MCD range from 0.47 to 0.60.

compounds from manure-rich wastewater, which is stored and used as a fertilizer at both dairy sites. At some locations, nitrification has been followed by denitrification. Prior to nitrification, cow manure likely starts out with a bulk $\delta^{15}\text{N}$ value close to 5‰, but is enriched in ^{15}N to varying degrees due to volatile loss of ammonia, resulting in $\delta^{15}\text{N}$ values of 10–22‰ in nitrate derived from manure (33, 34). Culture experiments have shown that nitrification reactions typically combine 2 oxygen atoms from the local pore water and one oxygen atom from atmospheric O_2 (35, 36), which has a $\delta^{18}\text{O}$ of 23.5‰ (37). Different ratios of oxygen from water and atmospheric O_2 are possible for very slow nitrification rates and low ammonia concentrations (38), however for dairy wastewater we assume that the 2:1 relation gives a reasonable prediction of the starting $\delta^{18}\text{O}$ values for nitrate at the two dairies based on the average values for $\delta^{18}\text{O}$ of groundwater at each site (–12.6‰ at KCD and –9.9‰ at MCD). Based on this approach, the predicted initial values for $\delta^{18}\text{O}$ in nitrate are –0.7‰ at KCD and 1.1‰ at MCD. Samples with the lowest nitrate $\delta^{15}\text{N}$ values have $\delta^{18}\text{O}$ values in this range, and are consistent with nitrate derived from manure. There is no strong evidence for mixing with nitrate from synthetic nitrogen fertilizers, which are used occasionally at both sites, but typically have low $\delta^{15}\text{N}$ values (0–5‰) and $\delta^{18}\text{O}$ values around 23‰ (39).

Denitrification drives the isotopic composition of the residual nitrate to higher $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values. The stable isotopes of nitrogen are more strongly fractionated during denitrification than those of oxygen, leading to a slope of approximately 0.5 on a $\delta^{18}\text{O}$ vs $\delta^{15}\text{N}$ diagram (34). Nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values at individual KCD multilevel well sites are positively correlated with calculated slopes ranging from 0.47 to 0.60; the slope of first encounter well data at MCD is 0.66 (Figure 3). These nitrate $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values indicate that denitrification is occurring at both sites. Because a wide range of fractionation factors are known to exist for this process (40), it is not possible to determine the extent of denitrification using only the isotopic compositions of nitrate along a denitrification trend, even when the initial value for manure-derived nitrate can be measured or calculated.

Extent of Denitrification. The concentrations of excess N_2 and residual nitrate can be combined with the isotopic composition of nitrate in order to characterize the extent of denitrification. In an ideal system, denitrification leads to a regular decrease in nitrate concentrations, an increase in excess N_2 , and a Rayleigh-type fractionation of N and O isotopes in the residual nitrate (Figure 4). In the Rayleigh fractionation model (41) the isotopic composition of residual nitrate depends on the fraction of initial nitrate remaining in the system ($f = C/C_{\text{initial}}$), the initial $\delta^{15}\text{N}$, and the fractionation factor (α) for denitrification:

$$\delta^{15}\text{N} = (1000 + \delta^{15}\text{N}_{\text{initial}}) f^{(\alpha-1)} - 1000$$

The fractionation factor α is defined from the isotopic ratios of interest ($R = ^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$):

$$\alpha = \frac{(R)_{\text{Product}}}{(R)_{\text{Reactant}}}$$

This fractionation can also be considered as an enrichment factor (ϵ) in ‰ units using the approximation $\epsilon \approx 1000 \ln \alpha$. The extent of denitrification can be calculated as $1 - f$. Rather than relying on an estimate of initial nitrate concentration, the parameter f is determined directly using field measurements of excess N_2 in units of equivalent reduced NO_3^- :

$$f = C_{\text{NO}_3^-} / (C_{\text{NO}_3^-} + C_{\text{excess N}_2})$$

Heterogeneity in groundwater systems can often complicate the interpretation of contaminant degradation using a Rayleigh model (42). Denitrified water retains a proportion of its excess N_2 concentration (and low values of f) during mixing, but the isotopic composition of nitrate may be disturbed by mixing since denitrified waters contain extremely low concentrations of nitrate (<1 mg/L). The sample from 1S with a f value close to zero and a $\delta^{15}\text{N}$ value of 7.6‰ was likely denitrified and is one example of this type of disturbance. However, in general, groundwater samples from the same multilevel well sites at KCD fall along similar Rayleigh fractionation curves, indicating that the starting isotopic composition of nitrate and the fractionation factor of denitrification vary across the site (Figure 4).

Values of $\delta^{15}\text{N}$ and f calculated from nitrate and excess N_2 fall along Rayleigh fractionation curves with enrichment factors (ϵ) ranging from –57‰ to –7‰ for three multilevel well sites at KCD and first encounter wells at MCD. As expected for denitrification, the enrichment factors indicated for oxygen are roughly half of those for nitrogen. The magnitude of these enrichment factors for N in residual nitrate are among the highest reported for denitrification, which typically range from –40‰ to –5‰ (34, 40). Partial gas loss near the water table interface at MCD could potentially increase the value of f , resulting in larger values of ϵ . Gas loss is unlikely to affect fractionation factors at KCD since most excess N_2 is produced well below the water table. Considering the large differences observed for denitrification fractionation factors within and between the two dairy sites, it is not sufficient to estimate fractionation factors for denitrification at dairies based on laboratory-derived values or field-derived values from other sites. The appropriate fractionation factors must be determined for each area, and even then the processes of mixing and gas loss must be considered in the relation between isotopic values and the extent of denitrification. Nevertheless, direct determination of the original amount of nitrate using dissolved N_2 values significantly improves our ability to determine the extent of denitrification in settings where the initial nitrate concentrations are highly variable.

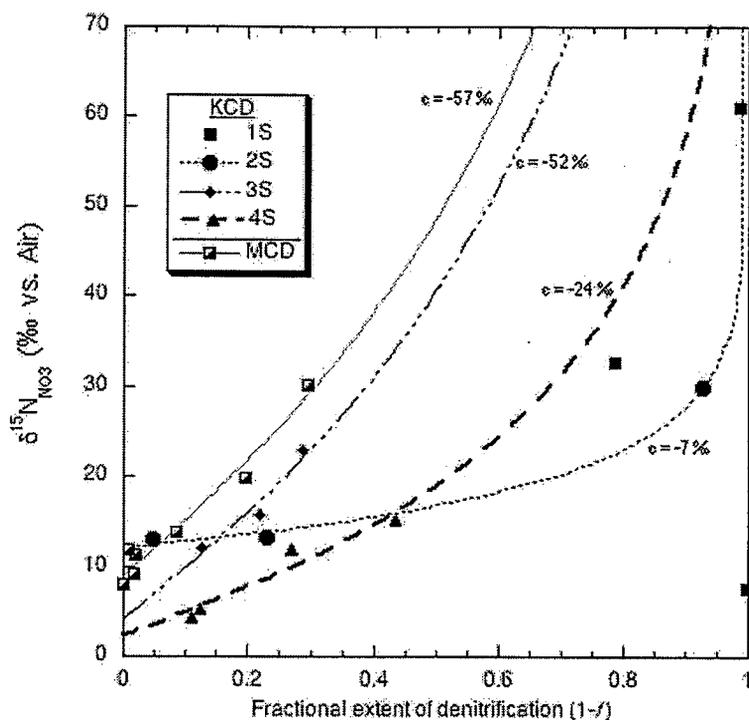


FIGURE 4. Nitrate $\delta^{15}\text{N}$ values plotted against the fractional extent of denitrification ($1 - f$) based on excess N_2 and residual nitrate. Enrichment factors (ϵ) are calculated by fitting the Rayleigh fractionation equation to data from three multilevel well sites at KCD and wells at MCD.

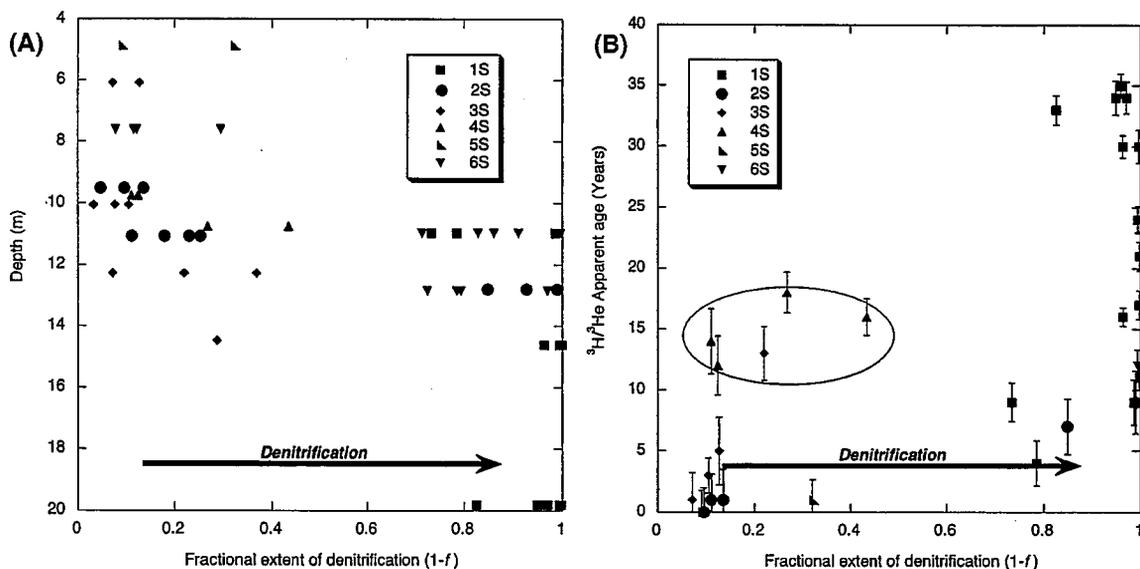


FIGURE 5. Sample depth (A) and $^3\text{H}/^3\text{He}$ apparent age (B) plotted against the fractional extent of denitrification ($1 - f$). Samples at two sites have experienced less denitrification than is typical for samples with $^3\text{H}/^3\text{He}$ apparent age > 8 years (circled, see text).

Time Scale of Denitrification. Modern water (i.e., groundwater containing measurable tritium) is found at all multilevel wells completed in the upper aquifer at KCD, the deepest of which is 20 m BGS. The upper aquifer below KCD has $^3\text{H}/^3\text{He}$ apparent ages of < 35 years. At well 1D1 (54 m BGS), the lower aquifer has no measurable NO_3^- and tritium below 1 pCi/L, indicating a groundwater age of more than 50 years. The sum of nitrate and excess N_2 is highest in the young, shallow dairy waters at KCD. Samples with $^3\text{H}/^3\text{He}$ ages > 29 years were below the MCL for nitrate prior to denitrification. These results are consistent with an increase in nitrate loading

at the surface, which followed the startup of KCD operations in the early 1970s.

The extent of denitrification at KCD is related to both depth and groundwater residence times based on $^3\text{H}/^3\text{He}$ apparent ages (Figure 5). There is a sharp transition from high nitrate waters to denitrified waters between 11 and 13 m depth across the KCD site. This transition is also related to the apparent age of the groundwater, as the high nitrate waters typically have apparent ages of between 0 and 5 years, and most samples with ages greater than 8 years are significantly or completely denitrified. There are five samples

that do not follow this pattern. These outliers are from sites 3S and 4S where the shallow groundwater has much higher $^3\text{H}/^3\text{He}$ apparent ages due to slow movement around clay zones at the screened intervals for these samples. The existence of older water that is not significantly impacted by denitrification indicates that it is the physical transport of water below the transition from oxic to anoxic conditions rather than the residence time that governs denitrification in this system.

At the MCD site, groundwater $^3\text{H}/^3\text{He}$ apparent ages indicate fast transit rates from the water table to the shallow monitoring wells. Most of the first encounter wells have apparent ages of <3 years, consistent with the hydraulic analysis presented by Harter et al. (5). The very fast transit times to the shallow monitoring wells at MCD allow for some constraints on minimum denitrification rates at this site. Based on the comparison of the calculated ages with the initial tritium curve, these shallow wells contain a negligible amount of old, ^3H -decayed water. In shallow wells near lagoons (e.g., W-16 and V-21), the observed excess N_2 (equivalent to 71 and 40 mg/L of reduced NO_3^-) accumulated over a duration of less than 1 year, indicating that denitrification rates may be very high at these sites. Complete denitrification of groundwater collected from well W-98 (excess N_2 equivalent to 51 mg/L NO_3^-) was attained within approximately 31 years, but may have occurred over a short period of time relative to the mean age of the water.

Occurrence of Denitrification at Dairy Sites. The depth at which denitrified waters are encountered is remarkably similar across the KCD site. This transition is not strongly correlated with a change in sediment texture. The denitrified waters at all KCD wells coincide with negative ORP values and generally low dissolved O_2 concentrations. Total organic carbon (TOC) concentration in the shallow groundwaters range from 1.1 to 15.7 mg/L at KCD, with the highest concentrations of TOC found in wells adjacent to lagoons. The highest concentrations of excess N_2 are found in nested well-set 2S, which is located in a field downgradient from the lagoons. However, sites distal to the lagoons (3S and 4S) that are apparently not impacted by lagoon seepage (43) also show evidence of denitrification, suggesting that direct lagoon seepage is not the sole driver for this process.

The chemical stratification observed in multilevel wells at the KCD site demonstrates the importance of characterizing vertical variations within aquifers for nitrate monitoring studies. Groundwater nitrate concentrations are integrated over the high and low nitrate concentration zones by dairy water supply wells, which have long screened intervals from 9 to 18 m BGS. Water quality samples from these supply wells underestimate the actual nitrate concentrations present in the uppermost oxic aquifer. Similarly, first encounter monitoring wells give an overestimate of nitrate concentrations found deep in the aquifer, and thus would miss entirely the impact of saturated zone denitrification in mitigating nitrate transport to the deep aquifer.

Monitoring wells at MCD sample only the top of the aquifer, so the extent of denitrification at depth is unknown, except for the one deep supply well (W98), which has less than 1 mg/L nitrate and an excess N_2 content consistent with reduction of 51 mg/L NO_3^- to N_2 . This supply well would be above the MCL for nitrate without the attenuation of nitrate by denitrification. The presence of ammonium at several of the wells with excess N_2 indicates a component of wastewater seepage in wells located near lagoons, where mixing of oxic waters with anoxic lagoon seepage may induce both nitrification and denitrification. Wells that are located in the surrounding fields have high NO_3^- concentrations, and do not have any detectable excess N_2 , a result consistent with mass-balance models of nitrate loading and groundwater nitrate concentration (5).

While dairy operations seem likely to establish conditions conducive to saturated zone denitrification, the prevalence of the phenomenon is not known. Major uncertainties include the spatial extent of anaerobic conditions, and transport of organic carbon under differing hydrogeologic conditions and differing nutrient management practices. Lagoon seepage may also increase the likelihood of denitrification in dairy aquifers. The extent to which dairy animal and field operations affect saturated zone denitrification is an important consideration in determining the assimilative capacity of underlying groundwater to nitrogen loading associated with dairy operations.

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Supporting Information Available

A table of chemical, isotopic, and dissolved gas results from this study, a plot of apparent age with depth, and detailed descriptions of the study sites. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supporting Information

Singleton et al, Saturated Zone Denitrification....

Supporting Information for “Saturated Zone Denitrification: Potential for Natural

Attenuation of Nitrate Contamination in Shallow Groundwater Under Dairy

Operations” by M. J. Singleton^{1*}, B. K. Esser¹, J. E. Moran¹, G. B. Hudson¹, W. W.

McNab², and T. Harter³

Contents: 7 Pages, 1 Figure, and 1 Table

Description of Dairy Sites

Study Site 1:

Study Site #1 is located at a dairy operation in Kings County, CA (KCD). Manure management practices employed at KCD, with respect to corral design, runoff capture and lagoon management are typical of practices employed at other dairies in the region. KCD has close to the 1000-cow average for dairies in the area, and operates three clay-lined wastewater lagoons that receive wastewater after solids separation. Wastewater is used for irrigation of 500 acres of forage crops (corn and alfalfa) on the dairy and on neighboring farms; dry manure is exported to neighboring farms.

KCD is located in the Kings River alluvial fan, a sequence of layered sediments transported by the Kings River from the Sierra Nevada to the low lying southern San Joaquin Valley of California (1, 2). The site overlies an unconfined aquifer, which has been split into an upper aquifer from 3m to 24m below ground surface (BGS) and a lower aquifer (>40 m BGS) that are separated by a gap of unsaturated sediments. Both aquifers are predominantly composed of unconsolidated sands with minor clayey sand layers. The lower unsaturated gap was likely caused by intense regional groundwater pumping, and a well completed in this unsaturated zone has very low gas pressures. There are no persistent gradients in water table levels across the KCD site, but in general, regional groundwater flow is from the NW to SE due to topographic flow on the Kings River fan. The water table is located about 5 m BGS. Local recharge is dominated by vertical fluxes from irrigation, and to a lesser extent, leakage from adjacent unlined canals. Transient cones of depression are induced during groundwater pumping from dairy operation wells.

The regional groundwater is highly impacted by agricultural activities and contains elevated concentrations of nitrate and pesticides (3, 4).

KCD was instrumented with five sets of multi-level monitoring wells and one “up-gradient” well near an irrigation canal. These wells were installed in 2002, and sampled between Feb. 2002 and Aug. 2005. The multi-level wells have short (0.5 m) screened intervals in order to detect heterogeneity and stratification in aquifer chemistry. One monitoring well was screened in the lower aquifer, 54m BGS. The remaining monitoring wells are screened in the upper aquifer from 5m to 20m BGS. In addition, there are eight dairy operation wells that were sampled over the course of this study. These production wells have long screens, generally between 9 to 18 meters below ground surface (BGS).

Study Site 2:

The second dairy field site is located in Merced County, CA. The Merced County dairy (MCD) lies within the northern San Joaquin Valley, approximately 160 km NNW from the KCD site. The site is located on the low alluvial fans of the Merced and Tuolumne Rivers, which drain the north-central Sierra Nevada. Soils at the site are sand to loamy sand with rapid infiltration rates. The upper portion of the unconfined alluvial aquifer is comprised of arkosic sand and silty sand, containing mostly quartz and feldspar, with interbedded silt and hardpan layers. Hydraulic conductivities were measured with slug tests and ranged from 1×10^{-4} m/s to 2×10^{-3} m/s with a geometric mean of 5×10^{-4} m/s (5). Regional groundwater flow is towards the valley trough with a

gradient of approximately 0.05% to 0.15%. Depth to groundwater is 2.5 m to 5 m BGS. The climate is Mediterranean with annual precipitation of 0.5 m, but groundwater recharge is on the order of 0.5–0.8 m per year with most of the recharge originating from excess irrigation water (3). Transit times in the unsaturated zone are relatively short due to the shallow depth to groundwater and due to low water holding capacity in the sandy soils. Shallow water tables are managed through tile drainage and groundwater pumping specifically for drainage. The MCD site is instrumented with monitoring wells that are screened from 2-3 m BGS to a depth of 7-9 m BGS. The wells access the upper-most part of the unconfined aquifer, hence, the most recently recharged groundwater (6). Recent investigations showed strongly elevated nitrate levels in this shallow groundwater originating largely from applications of liquid dairy manure to field crops, from corrals, and from manure storage lagoons (6). For this study, a subset of 18 wells was sampled. A deep domestic well was also sampled at MCD. This domestic well is completed to 57 m BGS, and thus samples a deeper part of the aquifer than the monitoring well network.

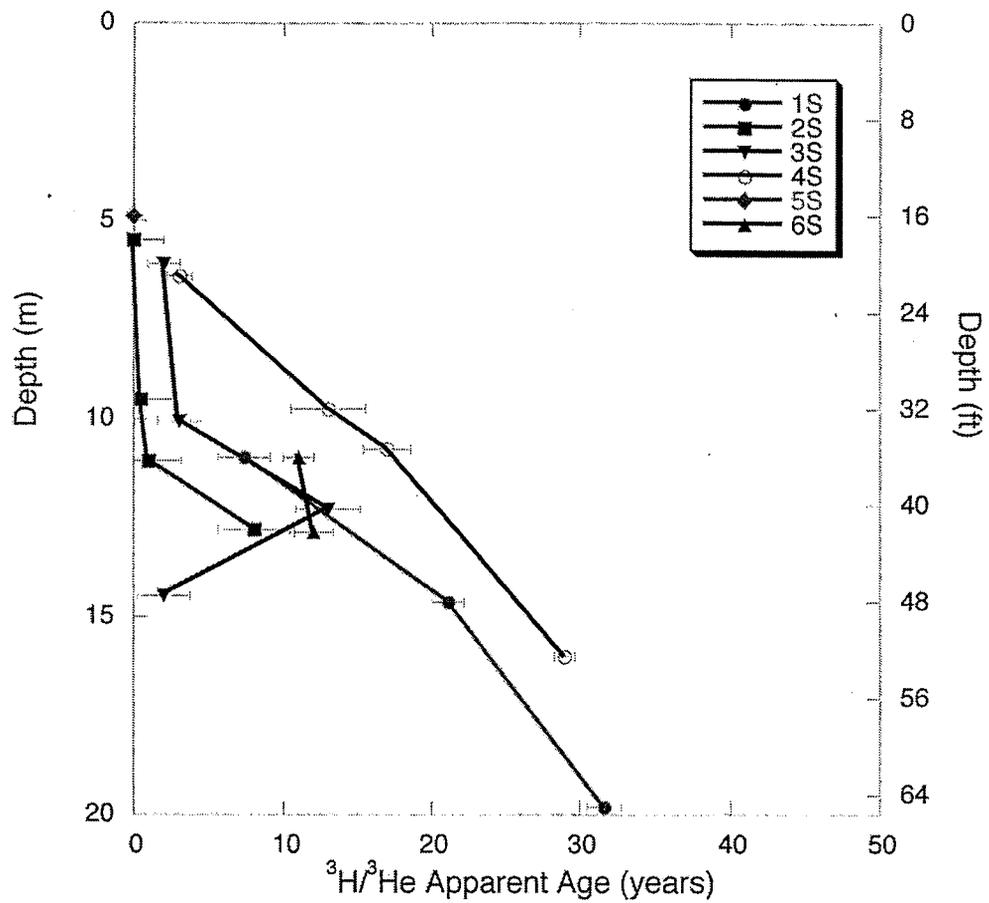


Figure S1. Groundwater $^3\text{H}/^3\text{He}$ apparent ages from multilevel monitoring wells at KCD. Error bars show analytical error.

Table S1. Chemical, dissolved gas, and isotopic compositions for multilevel groundwater monitoring wells and lagoons. Average values are given for wells sampled more than once. Excess N₂ values in bold are fully constrained by noble gas determinations of excess air and recharge temperature.

Site	Depth of multi-level well (m)	Cl ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	NH ₄ ⁺ (mg/L)	ORP	DO (mg/L)	TOC (mg/L)	δ ¹⁸ O H ₂ O (‰ SMOW)	δ ¹⁵ N NO ₃ ⁻ (‰ Air)	δ ¹⁸ O NO ₃ ⁻ (‰ SMOW)	³ H/ ² He age (yr)	³ H/ ² He age (yr)	Excess air determined from Ne (cc STP/g)	Recharge Temp. from Xe (°C)	+/- (°C)	³ H pCi/L	+/- (pCi/L)	N ₂ /Ar	
KCD-CANAL-1		1.5	1.2	0.2		10.0		-12.9								13.3	0.6	68	
KCD-LAGOON-1		304.5	28.6	360.8		0.4	480.0	-10.2										58	
KCD-LAGOON-2		265.2	13.9	292.1		0.5	490.0	-10.0										41	
KCD-LAGOON-3		212.2	22.4	181.3		0.5	420.0	-9.9										41	
KCD-ID1	54.3	1.9	0.2	<0.1	-264	0.2	0.8	-13.7	7.1		>50		3.40E-03	15	1.2	0.5	0.1	41	
KCD-IS1	6.7	166	206.0	166	166	3.5	2.5	-12.7	46.9	18.8	7.3	1.8	<1E-4	16	1.1	32.0	1.2	46	
KCD-IS2	11.0	52.5	11.1	0.3	-79	0.4	2.5	-12.8	7.6		21.1	1.1	2.82E-03	14	1.1	1.1	1.2	62	
KCD-IS3	14.6	36.0	0.5	1.3	-164	0.5	1.3	-12.9	7.6		31.7	1.1	4.02E-03	16	1.1	28.3	1.1	46	
KCD-IS4	19.8	9.8	0.4	2.5	-196	0.5	1.1	-13.3			0.0	2.0	1.70E-03	19	1.0	21.9	0.9	39	
KCD-2S1	5.5	107.7	144.5	<0.1	84	0.7	4.2	-12.3	13.1	-0.2	0.5	2.2	1.78E-03	22	1.1	19.5	0.8	49	
KCD-2S2	9.5	95.0	187.2	0.6	62	1.7	3.0	-12.1	13.2	0.2	1.0	2.1	<1E-4	21	1.1	19.3	0.8	62	
KCD-2S3	11.1	101.1	178.2	0.1	149	0.5	1.8	-12.4	29.9	2.4	8.0	2.4	<1E-4	23	1.8	19.8	0.8	100	
KCD-2S4	12.8	72.7	7.1	1.0	0	1.2	5.3	-11.7	14.5		2.0	1.0	1.42E-03	19	1.1	17.8	0.7	46	
KCD-3S1	6.1	170.4	203.1	0.4	0	1.2	5.3	-11.7	14.5		2.0	1.0	1.42E-03	19	1.1	17.8	0.7	46	
KCD-3S2	10.1	255.6	273.6	0.5	72	2.3	9.0	-11.9	15.8	5.2	3.0	1.4	6.35E-04	21	1.1	21.2	0.9	49	
KCD-3S3	12.3	162.7	167.8	0.5	107	1.2	9.0	-11.9	15.8	5.2	3.0	1.4	6.35E-04	21	1.1	21.2	0.9	49	
KCD-3S4	14.5	194.0	136.4	<0.1	79	1.0	5.6	-11.8	8.6	2.2	3.0	0.8	3.35E-04	20	1.0	18.6	0.8	53	
KCD-3S5	6.4	127.0	83.3	<0.1	79	1.0	5.6	-11.8	8.6	2.2	3.0	0.8	3.35E-04	20	1.0	18.6	0.8	53	
KCD-4S1	9.8	32.1	125.4	0.4	-16	0.8	1.1	-11.8	4.7	2.3	13.0	2.2	5.07E-03	18	1.3	20.3	0.8	51	
KCD-4S2	10.8	42.3	77.1	0.5	27	0.9	1.1	-12.0	13.5	6.1	17.0	1.6	3.54E-03	19	1.2	22.7	0.9	60	
KCD-4S3	16.0	35.0	0.9	1.8	-161	0.5	3.5	-13.0	18.9	1.8	<1	29.0	<1E-4	18	1.0	46.5	1.7	61	
KCD-4S4	4.9	14.5	35.4	1.3	37	0.5	1.5	-13.4	18.9	1.8	<1	29.0	<1E-4	18	1.0	46.5	1.7	61	
KCD-5S1	12.9	129.3	42.7	20.4		1.0	15.7	-11.9	12.1		12.0	1.3	<1E-4			29.1	1.1	70	
KCD-6S2	11.0	140.6	10.1	3.2		1.2	14.6	-11.8	12.1		11.0	1.0	<1E-4			33.3	1.2	67	
KCD-6S3	7.6	129.5	159.3	0.9		1.9	6.7	-11.6	19.0	7.7			2.13E-04			33.3	1.2	67	
KCD-NW-01	9-18	140.8	114.7	1.9		1.3		-12.0	15.0							35.9	1.3	51	
KCD-NW-02	9-18	163.4	75.2	3.4				-12.0	18.2							17.0	0.9	71	
KCD-NW-03	9-18	100.3	67.2	<0.1				-13.7			>50		7.72E-04	12	0.9	0.2	0.2	61	
KCD-NW-04	9-18	2.8	2.0	<0.1				-12.2								22.9	1.2	61	
KCD-NW-05	9-18	92.8	48.6	2.6				-12.7								24.8	1.4	57	
KCD-NW-06	9-18	52.6	91.0	<0.1				-12.4								30.4	1.3	57	
KCD-SW-02	9-18	45.1	29.2	1.9		1.5		-12.4											
KCD-SW-03	9-18	165.5	25.8	<0.1		3.8		-10.9								19.7	0.8	53	
KCD-SW-07	9-18	184.1	116.6	2.3															
KCD-SW-08	9-18	184.1	116.6	2.3															
MCD-LAGOON		514.0	<0.1	691.8		5.6	12.7	-9.3	13.9	7.4	12.0	1.7	<1E-4	25	1.2	36.0	1.4	62	
MCD-V-01	7.0	317.8	425.1	<0.1	111	5.6	12.7	-9.3	13.9	7.4	12.0	1.7	<1E-4	25	1.2	36.0	1.4	62	
MCD-V-14	7.6	71.4	316.0	<0.1			5.8	-10.7	11.2	1.7	2.0	2.9	1.26E-03	18	1.0	12.4	0.5	41	
MCD-V-18	6.1	77.2	195.5	1.7	193	3.3	8.1	-9.1	10.1	-0.5	<1					12.2	0.5	39	
MCD-V-21	9.1	145.5	163.1	<0.1	147	1.4	22.6	-10.5	19.9	9.2	<1					15.3	0.6	61	
MCD-V-24	9.1	30.2	201.5	<0.1	161	7.0	5.4	-10.5	7.4	-0.7	<1		4.31E-04	20	1.0	13.8	0.6	37	
MCD-V-95	7.0	73.0	303.2	2.4			12.2	-9.1	10.3	0.4	1.0	2.1	<1E-4	19	1.0	14.5	0.6	39	
MCD-W-02	7.0	226.1	2.0	148.5		0.6	12.7	-10.5								17.9	0.7	121	
MCD-W-03	7.0	82.2	341.8	0.7		0.8	14.5	-10.5								13.7	0.6	45	
MCD-W-05	7.0	48.3	230.6	<0.1				-10.7	6.8							14.5	0.8	39	
MCD-W-10	9.1	55.5	426.1	<0.1	171	0.7	9.1	-10.3	9.1	0.0	3.0	3.4	2.52E-03	19	1.1	13.5	0.6	44	
MCD-W-16	9.1	298.9	6.1	113.9	176	0.7	9.1	-8.1			<1	0.7	<1E-4	19	1.1	18.9	0.9	131	
MCD-W-17	9.1	136.9	171.7	26.7	208	0.7	9.8	-9.4	30.2	13.1	2.0	2.8	1.65E-03	20	1.0	13.9	0.5	43	
MCD-W-23	9.1	80.9	356.1	1.9	121	1.1	10.4	-10.2			1.0	2.3	1.23E-03	17	0.8	16.3	0.9	38	
MCD-W-30	9.1	49.1	324.8	<0.1				-9.9	5.3		<1		1.82E-03	17	0.8	15.9	0.7	40	
MCD-W-31	9.1	40.8	187.9	<0.1				-10.9	8.0		<1		1.82E-03	17	0.8	13.7	0.7	41	
MCD-W-34	7.3	63.4	185.6	<0.1				-10.8	7.9		<1		1.52E-03	17	0.8	15.3	0.8	41	
MCD-W-35	7.3	159.6	304.4	<0.1				-9.7	11.8		<1		1.76E-03	18	1.0	21.8	0.9	64	
MCD-W-98	57	69.6	0.4	<0.1		2.1		-10.6			31.0	0.6	1.76E-03	18	1.0	21.8	0.9	64	

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